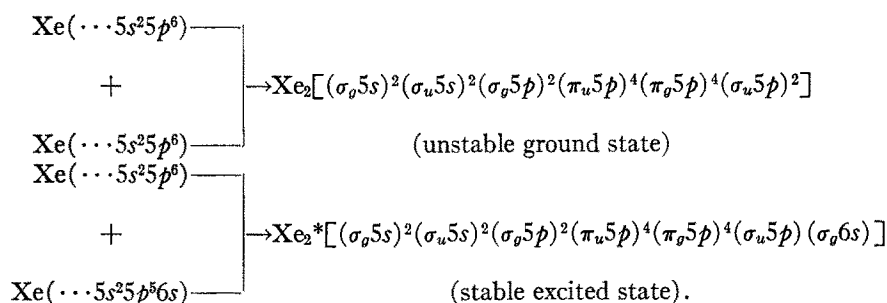


induction period is not made and  $\tau$  is used throughout this paper.

### DISCUSSION

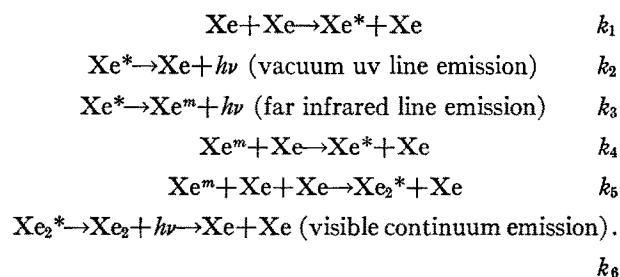
In a recent publication of the results of a study of the luminosity behind shock waves in argon,<sup>8</sup> it was suggested that the induction period is a consequence of a delay in ionization of the argon. The mechanism proposed involves the ionization of impurities, Im, by collision with argon atoms directly behind the shock front:  $A + \text{Im} \rightarrow A + \text{Im}^+ + e^-$ . The electrons produced in this process have very little kinetic energy. The induction period is attributed to the time necessary for these electrons to suffer many more collisions so that a sufficient fraction of them will acquire the energy necessary to ionize argon. This is followed by:  $A + e^- (15.7 \text{ ev}) \rightarrow A^+ + 2e^-$ . Finally, visible continuum emission is presumed to result from the recombination of electrons and argon ions.

This mechanism leaves unanswered the question of the origin of the visible continuum emission from rare gases under conditions where the degree of ionization is very low (e.g., transformer discharges, microwave discharges, weak shock waves). It can be shown that for the weakest shock condition listed in Table I,



The ground state of the molecule has a net of no bonds and a stable molecule cannot be formed. In the case of the excited state, however, there is one stable bond if the configuration terminates at  $(\pi_g 5p)^4$ . Thereafter, the  $(\sigma_u 5p)$  electron is antibonding and the  $(\sigma_g 6s)$  electron is bonding. These cancel each other and the net effect is the formation of a stable molecule having a single bond.

The following mechanism is proposed for visible continuum emission in xenon but may also be valid for other rare gases.



the maximum degree of ionization is about 0.2% and for the strongest shock, it is about 5%. Furthermore, it was shown recently<sup>14,15</sup> that atomic or molecular collisions are more important than electron impact in producing emission behind shock waves.

On the other hand, the discovery by Tanaka<sup>10-12</sup> of a molecular band system associated with the resonance line of each of the rare gases presents an alternative possibility. The potential energy curve for two approaching ground state rare gas atoms is almost entirely repulsive. At most, there is a van der Waals attractive well of about 0.01 ev. If, as suggested by Tanaka, a stable molecule can be formed by interaction of a ground-state atom with an atom in the first excited state, then dissociative transitions from this stable molecular state to the unstable ground state could result in continuum emission in the visible. An additional interesting possibility is that the metastable atomic state lying slightly below the resonance state becomes highly populated. Atoms have relatively long lifetimes in this state and this would increase the probability of molecule formation by collision with ground state atoms. The electronic configurations of the ground and excited states of the xenon molecule may be represented as follows:

Here,  $\text{Xe}^m$  represents the metastable state at 8.3 ev,  $\text{Xe}^*$  indicates any excited state which can combine with the metastable state but is probably chiefly the resonance state at 8.4 ev, and  $\text{Xe}_2^*$  is the lowest lying, stable molecular state. At the peak of continuum emission, the concentration of  $\text{Xe}_2^*$  is in a steady state and  $d(\text{Xe}_2^*)/dt = 0$ . Simple considerations indicate that  $\text{Xe}^m$  and  $\text{Xe}^*$  concentrations are also in a steady state at this time. Then,  $d(\text{Xe}^m)/dt = 0$  and  $d(\text{Xe}^*)/dt = 0$  and solving for  $(\text{Xe}^m)$  gives

$$(\text{Xe}^m) = \frac{[k_3/(k_2 + k_3)]k_1(\text{Xe})}{[k_2/(k_2 + k_3)]k_4 + k_5(\text{Xe})}.$$

Reaction (3) violates the Laporte rule and cannot occur as an electric dipole transition. It can occur, however, as a magnetic dipole transition. In this case, the transition probability is about  $10^{-5}$  of that of an

<sup>14</sup> A. R. Fairbairn and A. G. Gaydon, Proc. Roy. Soc. (London) **A239**, 464-475 (1957).

<sup>15</sup> J. G. Clouston and A. G. Gaydon, Nature **180**, 1342-1344 (1957).

electric dipole transition.<sup>16</sup> In fact, magnetic dipole transitions have been observed in Xe with intensities about  $10^{-3}$  of the intensities of the strongest Xe lines.<sup>17</sup> Therefore,  $k_2 \gg k_3$ . Furthermore, the bimolecular reaction (4) can be expected to be very much faster than the termolecular reaction (5). Applying these conditions results in the simplified expression,

$$(Xe^m) = k_1 k_3 (Xe) / k_2 k_4.$$

The net rate of  $Xe_2^*$  production is

$$d(Xe_2^*)/dt = k_5 (Xe^m) (Xe)^2 - k_6 (Xe_2^*),$$

and substituting for  $(Xe^m)$ ,

$$d(Xe_2^*)/dt = k_1 k_3 k_5 (Xe)^3 / k_2 k_4 - k_6 (Xe_2^*).$$

It is clear that, since reaction (6) is very rapid, any measure of the rate of  $Xe_2^*$  production will appear to be third order and the time for any given fraction of the reaction to occur will be proportional to

$$k_2 k_4 T^2 / k_1 k_3 k_5 p_{Xe}^2$$

where  $p_{Xe}$  is the pressure of Xe. This will also be proportional to the induction period  $\tau$  of Table I which is measured between peaks in Fig. 1(b). Reactions (2), (3), and (5) occur without activation energy. Therefore,  $\tau = (\text{constant}) T^{3/2} \exp(E_a/kT) / p_{Xe}^2$  or in the subscript notation previously introduced,

$$\tau = (\text{constant}) T_1^{3/2} \exp(E_a/kT_1) p_1^2.$$

Here,  $E_a = E_1 - E_4$  which is just the energy of the metastable level. Making the substitution  $p_1 = (\text{constant}) p_0 T_1$  gives  $\tau = A \exp(E_a/kT_1) / p_0^2 T_1^{3/2}$  where  $A$  is a constant.

It can be seen, from the above, that a plot of  $\log(p_0^2 T_1^{3/2} \tau)$  against  $(\log e)/kT_1$  should give a straight line with slope equal to  $E_a$ . Such a plot of the data in Table I is shown in Fig. 2. The line drawn in was determined by the method of least squares and has a slope of 8.2 ev. This is in very good agreement with the energy of the metastable level of Xe which is 8.3 ev. Further evidence in favor of the proposed mechanism is found in a plot, similar to that in Fig. 2, of the data reported for argon.<sup>8</sup> In this case, the activation energy is about 11.5 ev in good agreement with the energy of the metastable state of argon.

It should be noted that the ionization-recombination mechanism<sup>8</sup> discussed earlier would be expected to lead to an activation energy which is equivalent to the ionization potential of the rare gas involved.

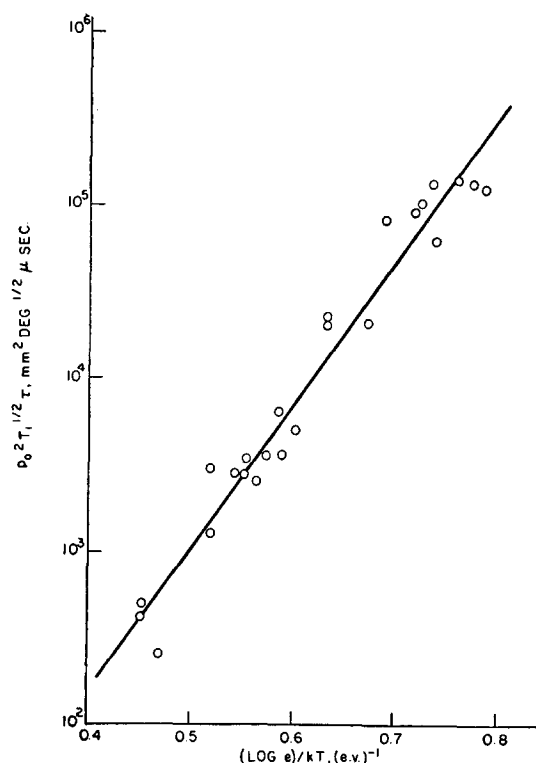


Fig. 2. Least square plot to determine the activation energy associated with the induction period for continuum emission in Xe.

If direct excitation to the metastable state from the ground state by collision of two Xe atoms is included in the mechanism presented here, essentially the same result is obtained. In the very unlikely case that direct excitation to the metastable state is highly favored over excitation to the resonance state, the activation energy will be about 0.1 ev less than the energy of the metastable level.

The reverse of reaction (4), namely, deactivation of resonance state atoms to metastable state atoms by collision, has been omitted from the mechanism. Although the rate constant for this reaction can be expected to be comparable to that of (4), it is more probable that a collision between a resonance state atom and a ground-state atom will result in excitation to the next higher level particularly since the average translational energy of Xe atoms in the temperature range studied is about 1 ev. The difference in energy between the resonance state ( $5p^56s$ ) and the next higher state ( $5p^56p$ ) is also about 1 ev.

The variation of continuum intensity with temperature and pressure might be expected to follow the third-order rate law developed here. Unfortunately, we were unable to confirm this. Intensity measurements were very poorly reproducible and seemed to be very strongly dependent upon the nature of the diaphragm burst. Furthermore, the relative populations of the various energy levels during the time of continuum emission in Fig. 1(b) will be temperature-

<sup>16</sup> G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944), p. 54.

<sup>17</sup> Thekaekara, Dieke, and Crosswhite, *Johns Hopkins Spectroscopic Report No. 12*, December, 1955.

and time-dependent. The determination of the temperature during continuum emission therefore cannot be made with any certainty. Even if it is assumed that ionization equilibrium exists at the peak of continuum emission, results are not in accord with the dependence of continuum intensity on the square of the equilibrium ion concentration predicted by Unsöld.<sup>2</sup>

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge valuable discussions with Y. Tanaka of the Air Force Cambridge Research Center and C. Kenty of the General Electric Company.

We are indebted to G. L. Brengelmann for photometry of the spectrum of the reflected shock in xenon.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 29, NUMBER 4

OCTOBER, 1958

## Thermodynamics of Nonstoichiometric Nickel Tellurides. II. Dissociation Pressures and Phase Relations of Tellurium-Rich Compositions\*

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(Received June 9, 1958)

Dissociation pressures of tellurium over liquid and solid nickel telluride solutions have been measured with a silica Bourdon gauge at compositions corresponding to  $\text{NiTe}_{1.6}$ ,  $\text{NiTe}_{1.7}$ ,  $\text{NiTe}_{1.8}$ ,  $\text{NiTe}_{2.0}$ , and  $\text{NiTe}_3$  at temperatures up to  $780^\circ$ . Modifications of the manometric technique are described which permit accuracies of 0.1 mm pressure and  $0.1^\circ$  at high temperatures with corrosive substances where the pressure is sensitive to impurities or to composition changes. The results, together with data on the vapor pressure of pure tellurium, define the partial molal free energies and entropies of tellurium and, together with direct eutectic temperature measurement, delineate features of the phase diagram for compositions with more than 60 atomic percent tellurium.

#### INTRODUCTION

THE interesting nature of the nickel/tellurium system, and an outline of the previous literature, have been presented in a previous paper,<sup>1</sup> which also reported the heat capacity and thermodynamic functions up to room temperature. The present research was undertaken as part of a continuing program directed toward the determination of zero-point entropies as a function of composition of nickel tellurides.

The equilibrium pressure of tellurium vapor over various compositions of nickel tellurides from 60 to 100 atomic percent tellurium was measured at temperatures up to  $780^\circ$ . These measurements determined the phase behavior over this region with the exception of the eutectic, which is almost degenerate in that the composition differs only very slightly from pure tellurium. The eutectic temperature and composition were determined directly.

#### EXPERIMENTAL

##### Vapor Pressure Measurement

Of the methods available for the measurement of vapor pressure, few are capable of being applied with

accuracy at high temperatures. Effusion methods are accurate, but are limited to pressures lower than about 0.1 mm. Dynamic methods in general are indirect and, therefore, subject to systematic errors; furthermore, they are difficult to apply to multicomponent substances where the pressure changes as the material is progressively vaporized. Static methods, on the other hand, are subject to errors from minute amounts of impurities, particularly those which are volatile and insoluble in the sample. In both cases there are other "difficulties and sources of error which increase exponentially with the temperature."<sup>2</sup> The present method is based on the use of a Bourdon gauge of vitreous silica used as a null instrument between the hot vapor to be measured and an inert gas, the pressure of the latter being measured on a conventional manometer. Such Bourdon gauges have been described in the literature<sup>3</sup> for measuring vapor pressure. The principal refinements and modifications concern methods of outgassing the apparatus; purifying the sample; insuring uniformity and accuracy of measurement of sample temperature; observing the deflections of the gauge

\* This work was submitted to the H. H. Rackham School of Graduate Studies in partial fulfillment of the requirements of the Ph.D. degree of R. E. Machol.

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<sup>1</sup> Westrum, Grønvald, Chou, and Machol, *J. Chem. Phys.* **28**, 497 (1958).

<sup>2</sup> O. Kubaschewski and E. L. Evans, *Metallurgical Thermodynamics* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 171.

<sup>3</sup> J. R. Partington, *An Advanced Treatise on Physical Chemistry* (Longmans, Green, and Company, London), Vol. 1 (1949), p. 565 ff; Vol. 2 (1951), pp. 233 ff, 234 f. Kubaschewski and Evans, reference 2, pp. 145-147. Cf. Phipps, Spealman, and Cooke, *J. Chem. Educ.* **12**, 321 (1935).